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Self-heating of coal: The diminishing reaction rate

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Abstract

Several models for the self-heating of coal resulting from the chemisorption of oxygen are investigated. All of the models investigated include the effect of a diminishing reaction rate. The various mathematical forms used to represent the diminishing part of the reaction are compared and a new formulation in the form of a generic power-law model is introduced. Results from the new model are compared with those obtained using previous models.

Keywords: Self-heating; Coal; Diminishing reaction rate; Chemisorption; Power-law model

1. Introduction

The mining process exposes a large surface area and therefore newly mined coal immediately begins chemisorbing oxygen and releasing heat [1] at a much more rapid rate than in the in situ state. This process is normally known as pre-oxidation for the period from mining until the coal is stockpiled. If the rate of heat generation in a coal stockpile exceeds the rate of heat removal from the boundaries, the temperature will rise, possibly up to the ignition point. During this process, the rate of oxygen chemisorption reduces with time, because the available reactive surface diminishes. This results in a diminishing rate of reaction, even when the reactant oxygen is abundant. Mathematical modeling of such systems presents a challenging task because of this special feature. Systems with diminishing reaction rates are of practical importance not only for coal, but also in materials like char, sawdust, wool, polypropylene, paper, fish meal and others [2–5].

Pre-oxidation in coal has been acknowledged for a long time (e.g. [6] and [7]), but there was no mathematical model of the process until Schmidt and Elder [1] experimentally derived the following equation:

$$\frac{\mathrm{dO_{ad}}}{\mathrm{d}t} = kt^{-\alpha} \qquad (1)$$

Here $\mathrm{O_{ad}}$ is the concentration of adsorbed oxygen and k and α are constants. Schmidt and Elder [1] determined a value of $\alpha = 0.2$, while later Beamish et al. [8] obtained $\alpha = 0.14$ for a different particle size and using a different (adiabatic) testing procedure.

Although several previous studies [2,3,9] successfully used (1) for modelling a diminishing reaction, it is not really a physically based mathematical model. In fact, the rate of oxidation is controlled by the reactive area, which in turn depends on the current level of adsorbed oxygen in the system. Thus it is better to represent the diminishing reaction of coal self-heating by an equation with a right hand side expressed as a function of $\mathrm{O_{ad}}$ rather than t, i.e. to replace Eq. (1) by

$$\frac{\mathrm{dO_{ad}}}{\mathrm{d}t} = F(\mathrm{O_{ad}}) \qquad (2)$$

The main purpose of the present paper is to show how to set up an equation with the form shown in (2) that can match the experimental data as well as Eq. (1), and to compare the results obtained by using (2) with those derived from (1). Previously Chen and Wake [4,5] recognized the need to modify Eq. (1), and presented an alternative form with a right hand side depending on $\mathrm{O_{ad}}$. However their derivation used (1) as a starting point and consequently the Arrhenius temperature dependence of their model may not be correct.

The present work will consider three models in detail:

(i) The model represented by Eq. (1) and its modifications (classical model).

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Nomenclature

A_0	Arrhenius pre-exponential facto (s^{-1})
C_{O_2}	oxygen concentration in gas phase ($kg\,m^{-3}$)
C_p	specific heat capacity ($kJ\,kg^{-1}\,K^{-1}$)
C_0	initial oxygen concentration in gas phase ($kg\,m^{-3}$)
E_a	activation energy ($J\,mol^{-1}$)
k	non-isothermal reaction rate, $k = A_0 \exp(-E_a/RT)$
k_0	isothermal reaction rate, $k_0 = A_0 \exp(-E_a/RT_0)$
n	reaction order
O_{ad}	concentration of adsorbed oxygen in coal ($kg\,kg^{-1}$)
O_D	representative value of O_{ad} ($kg\,kg^{-1}$)
O_0	initial concentration of adsorbed oxygen in coal ($kg\,kg^{-1}$)
Q	heat of reaction (Exothermicity) ($J\,kg^{-1}$)
r_{O_2}	reaction rate for consumption of oxygen ($kg\,s^{-1}\,m^{-3}$)
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
t	time (s)
t_{pr}	prior reaction time (s)
T	temperature (absolute) (K)

Greek symbols

β	new empirical constant for the diminishing rate low
δ_0	modified Frank–Kamenetskii parameter (see Eq. (40))
ε	reduced ambient temperature (see Section 5)
ϕ	porosity
γ	incomplete Gamma function
λ	constant (see Eq. (41))
θ	reduced excess temperature (see Eq. (36))
ρ	density ($kg\,m^{-3}$)
τ	time scale (s)

Subscripts

ad	adsorbed
coal	coal
O_2	Oxygen
∞	infinite
0	initial conditions (ambient conditions)

Superscript

*	non-dimensional form

(ii) A model of the type represented by Eq. (2) derived by Chen and Wake [4,5] (CW model).

(iii) A new power-law form for the right hand side of Eq. (2) (new model).

In addition some other versions of (2), such as the Elovich model, will be briefly discussed.

2. Diminishing reaction rate model

There are many different forms presented in the literature for the mathematical model of the oxidation of coal by chemisorption. Therefore, before concentrating on the diminishing aspect of the reaction a general formulation of the conservation equations governing self-heating of coal will be presented. Then a simplified model will be derived by neglecting changes in the oxygen concentration in the gas phase.

The reaction of oxygen chemisorbing on coal is assumed here to have the simple form:

$$C + O_2 \xrightarrow{k} \text{oxy-coal complex} + Q(\rightarrow \text{products}) \tag{3}$$

In fact the details of the reaction of oxygen with coal are complex (see [10,11] for example) and the reaction represented by (3) and the corresponding formulae used below are approximations. However past work on diminishing effects has been based on Eq. (3) and it will be assumed again here.

2.1. Conservation of oxygen in the pores

The equation for the conservation of the mass of oxygen in the pores is

$$\phi \frac{\partial C_{O_2}}{\partial t} = -r_{O_2} \tag{4}$$

This is a lumped parameter model that ignores variations in space resulting from advection and diffusion. Here ϕ is the porosity of coal, C_{O_2} is the oxygen concentration ($kg\,m^{-3}$ of gas) and r_{O_2} is the rate of chemisorption of oxygen ($kg\,s^{-1}\,m^{-3}$ of whole space, i.e. gas plus solid).

2.2. Conservation of adsorbed oxygen

Similarly the equation for the conservation of oxygen in the coal matrix is:

$$(1-\phi)\rho_{coal} \frac{\partial O_{ad}}{\partial t} = r_{O_2} \tag{5}$$

Here ρ_{coal} is the density of coal and O_{ad} is the mass fraction of adsorbed oxygen ($kg_{O_2}\,kg_{coal}^{-1}$).

2.3. Conservation of heat

The heat balance is:

$$(1-\phi)\rho_{coal}\, C_{p,coal} \frac{\partial T}{\partial t} = Q r_{O_2} \tag{6}$$

2.4. Rate of reaction

The key term in Eqs. (4)–(6) is the rate r_{O_2}. Because the reaction takes place on the surface of the coal particles it is appropriate to express it [12] in the form:

$$r_{O_2} = (1-\phi)\rho_{coal} O_D k f\left(\frac{O_{ad}}{O_D}\right)\left(\frac{C_{O_2}}{C_0}\right)^n \tag{7}$$

In (7) the density of coal ρ_{coal} converts a reaction rate in mass units (per kg of coal) into volume units (per m^3 of coal) and then the factor $(1-\phi)$ converts it to total volume units (per m^3 of coal plus pore space). The term $\mathrm{O_D}f(\mathrm{O_{ad}}/\mathrm{O_D})$ is a normalized form of the contribution of the diminishing effect to the overall reaction. Here $\mathrm{O_D}$ is a representative value for $\mathrm{O_{ad}}$, for example the initial value. The normalized form is used to allow simple non-dimensionalisation of (7) and related formulae. The term $(C_{\mathrm{O_2}}/C_0)^n$ corresponds to the contribution to the reaction of the changes in oxygen concentration in the pores. Here a general nth order reaction is assumed. Again a normalized form is used with C_0 being a typical concentration (for example the initial value).

In Eq. (7) k is the reaction rate coefficient. It is temperature dependent according to the Arrhenius equation:

$$k = A_0 \exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{8}$$

Combining (5), (7) and (8) gives:

$$\frac{\mathrm{dO_{ad}}}{\mathrm{d}t} = \mathrm{O_D} f\left(\frac{\mathrm{O_{ad}}}{\mathrm{O_D}}\right)\left(\frac{C_{\mathrm{O_2}}}{C_0}\right)^n A_0 \exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{9}$$

The assumption is usually made that the oxygen is abundant and therefore its concentration does not change significantly, i.e. $C_{\mathrm{O_2}} \approx C_0$. In this case (4) becomes redundant and (9) can be written as:

$$\frac{\mathrm{dO_{ad}}}{\mathrm{d}t} = \mathrm{O_D} f\left(\frac{\mathrm{O_{ad}}}{\mathrm{O_D}}\right) A_0 \exp\left(-\frac{E_\mathrm{a}}{RT}\right) \tag{10}$$

Note that (10) has the form given in (2) with:

$$F(\mathrm{O_{ad}}) = \mathrm{O_D} f\left(\frac{\mathrm{O_{ad}}}{\mathrm{O_D}}\right) A_0 \exp\left(-\frac{E_\mathrm{a}}{RT}\right) = k\mathrm{O_D} f\left(\frac{\mathrm{O_{ad}}}{\mathrm{O_D}}\right)$$

Similarly the conservation of heat, Eq. (6), can be written as:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{Q}{C_{p,\text{coal}}} F(\mathrm{O_{ad}}) \tag{11}$$

The aim now is to solve Eqs. (10) and (11) together with initial conditions:

$$\mathrm{O_{ad}}(0) = \mathrm{O_{ad0}}, \qquad T(0) = T_0$$

It should be noted that coal will always be pre-oxidised to some extent but the value of $\mathrm{O_{ad0}}$ will not be known and would be difficult to measure. Thus the initial condition $\mathrm{O_{ad0}} = 0$ that has been used sometimes in the past is not physically realistic.

In Section 3 below, the various forms previously proposed for $F(\mathrm{O_{ad}})$ are reviewed. In Section 4 the new power-law model is introduced and compared with previous work for the isothermal case. The non-dimensional heat equation is discussed in Section 5. Then in Sections 6–9 approximate analytical solutions for temperature–time relationships for the new model and previous models are obtained. A comparison of results for the various models is given in Section 10.

3. Previous diminishing reaction models

3.1. Elovich equation

The kinetics of chemisorption are often represented using the Elovich equation:

$$F(\mathrm{O_{ad}}) = a\mathrm{e}^{-b\mathrm{O}_{ab}} \tag{12}$$

Here a and b are empirical constants. This equation provides a simple graphical method for curve fitting. It has been applied extensively to chemisorption measurements from a variety of systems [12–14]. However it sometimes fails to match the experimental data [15], particularly at early times [16].

3.2. Time-dependent functions

Boddington et al. [2] recognised that the right hand side of Eq. (1) gives an infinite rate at $t = 0$ and replaced it with a well-behaved time-dependent function $kg(t)$, with $g(t)$ defined by:

$$g(t) = \frac{1}{(t+t_{\mathrm{pr}})^\alpha}, \quad t_{\mathrm{pr}} \geq 0, \quad 0 \leq \alpha < 1 \tag{13}$$

Here t_{pr} is the pre-oxidation time. Boddington et al. [2] gave values for α ranging from 0.3 to 0.7. Chen and Wake [4] used slightly smaller values ($\alpha = 0.2$ and 0.23) for coal. The value of t_{pr} may be small compared with the typical induction time (t) in coal stockpiles. Some authors [4,5] have assumed $t_{\mathrm{pr}} = 0$, accepting the singular behaviour at $t = 0$, and have used the simpler approximate form of Eq. (1).

Schmidt and Elder [1] introduced Eq. (1) but did not include temperature dependence in the reaction coefficient k. With $\alpha = 0.5$, Eq. (1) corresponds to the formula used in the theory of tarnishing surfaces where the depositing film grows at a rate inversely proportional to its thickness [18].

3.3. Schmal's formulae

Schmal et al. [12] and Schmal [13] proposed two different diminishing functions to model the influence of reduction in coal reactivity. These models included a first-order representation of oxygen consumption along with a diminishing rate and were solved numerically. The two forms used to represent the diminishing rate were:

(a) Linearly decreasing reaction rate.

$$F(\mathrm{O_{ad}}) = 1 - (\mathrm{O_{ad}}/s), \qquad \mathrm{O_{ad}} \leq s, \quad s = 0.01 \tag{14}$$

(b) Exponentially reducing reaction rate (similar to the Elovich equation).

$$F(\mathrm{O_{ad}}) = \exp(-\mathrm{O_{ad}}/s), \quad s = 0.0039 \tag{15}$$

As expected the inclusion of these diminishing terms slows the increase in temperature. However, Schmal et al. [12] concluded that the effect is small compared to the more significant influence of variations in porosity and wind velocity on the heating of coal stockpiles.

Later Schmal [13] used (15) with different values of s to investigate the influence of coal weathering on the maximum temperature rise in a coal stockpile. His results showed that for highly weathered coal ($s \leq 0.01$) spontaneous combustion could be averted.

3.4. Chen and Wake

Chen and Wake [4,5] started with Eq. (13), i.e. with the time-dependent rate used by Boddington et al. [2], and solved an isothermal problem to obtain t as a function of O_{ad} in the form:

$$t = \left[\frac{O_{ad}(1-\alpha)}{k} + t_0^{1-\alpha}\right]^{1/(1-\alpha)} \tag{16}$$

In deriving (16) they assumed $t_{pr} = 0$, but avoided the singularity at $t = 0$ by applying the initial conditions at time t_0 in the form $O_{ad}(t_0) = 0$. They later assumed $t_0 = 0$ and then substituted (16) back into (13) to obtain:

$$F(O_{ad}) = \frac{k}{[(1-\alpha)O_{ad}/k]^{\alpha/1-\alpha}} \tag{17}$$

It is not clear how Eq. (17), which was derived for an isothermal reaction, should be used for nonisothermal problems. In particular the appearance of the coefficient k in the denominator is an artifact of the method of derivation and may not be related to the physical basis of the mathematical model.

Chen and Wake [4] noted that a model using (17) reaches ignition in less time than a model based on (13) (i.e. the model of Boddington et al. [2,3]). While the present authors agree with Chen and Wake that having time-dependence in the rate equation is conceptually incorrect, in our opinion their derivation of (16) and (17) is still not sufficiently general. We offer an alternative approach in the next section.

Chen and Wake [5] proposed two further models for the diminishing reaction rate:

$$F(O_{ad}) = [1 + b(O_{ad})^m]^{-1}$$

and

$$F(O_{ad}) = \exp(-b(O_{ad})^m)$$

These models are quite similar to those proposed by Schmal et al. [12] (see Eqs. (14) and (15)).

4. Modified diminishing rate of reaction

In this section we will investigate several diminishing rate models and propose a new model. In order to compare all models on the same basis a non-dimensional formulation will be introduced. First we define non-dimensional variables as follows:

$$O^*_{ad} = \frac{O_{ad}}{O_D}, \qquad T^* = \frac{T}{T_0}, \qquad t^* = \frac{t}{\tau}$$

Here O_D is a typical oxygen concentration, T_0 is the initial temperature and τ is a characteristic time-scale for the problem.

Then the non-dimensional form of Eq. (9) becomes:

$$\frac{dO^*_{ad}}{dt^*} = k^* f(O^*_{ad}) \tag{18}$$

with

$$k^* = A^*_0 \exp\left(-\frac{E_a}{RT_0}\frac{1}{T^*}\right)$$

Here $A^*_0 = \tau A_0$.

We now present the three main models discussed in this paper (new model, classical model and CW model) and solve them for the isothermal case ($T = T_0$ or $T^* = 1$).

4.1. New model—power-law rate

We propose a power-law diminishing term in the non-dimensional form:

$$f(O^*_{ad}) = \left(\frac{b + O^*_{ad0}}{b + O^*_{ad}}\right)^{\beta} \tag{19}$$

This equation was derived in three stages. First from the past experimental data and past models such as Eq. (1) it is clear that:

$$f(O^*_{ad}) \propto (O^*_{ad})^{-\beta} \tag{20}$$

Secondly, to avoid singular behaviour at $O^*_{ad} = 0$ Eq. (20) was modified to the form:

$$f(O^*_{ad}) \propto (b + O^*_{ad})^{-\beta} \tag{21}$$

It will be shown later that this modification is equivalent to the addition of t_{pr} in (13). Finally (21) was normalized to give $f(O^*_{ad0}) = 1$ and thus (19) resulted. As pointed out above the initial condition $O^*_{ad} = 0$ is probably not physically realistic but nevertheless it has been used in the past and therefore it was decided that it was essential to use a form like Eq. (21) which remains well-behaved in the limit $O^*_{ad} \to 0$.

Eq. (19) is similar to the equation derived by Chen and Wake [3,4] (see (17)) but an important difference is that the parameter b is now a constant. Thus the temperature dependence of the reaction rate is included only in the Arrhenius term in the rate coefficient k^* and the diminishing term $f(O^*_{ad})$ is assumed to be independent of temperature. The parameters b and β are constants that can be related to the parameters used in previous models [2,4,5].

For the isothermal case, substitution of (19) into (18) gives:

$$\frac{dO^*_{ad}}{dt^*} = k^*_0 \left(\frac{b + O^*_{ad0}}{b + O^*_{ad}}\right)^{\beta} \tag{22}$$

With the initial condition:

$$O^*_{ad}(0) = O^*_{ad0} \tag{23}$$

This problem can be solved by separation and integration:

$$O^*_{ad} + b = (O^*_{ad0} + b)\left[1 + \frac{(\beta + 1)}{(O^*_{ad0} + b)}k^*_0 t^*\right]^{1/\beta+1} \tag{24}$$

4.2. Classical model—time-dependent rate

In order to compare our new model with the past work of Boddington et al. [2,3], Lacey and Wake [9] and Chen and Wake [4,5], we will now re-work their derivation using more general initial conditions. Using a non-dimensional and normalized version of (13) the isothermal model is:

$$\frac{\mathrm{dO}^*_{\mathrm{ad}}}{\mathrm{d}t^*} = k^*_0 \frac{1}{(1+t^*/t^*_{\mathrm{pr}})^{\alpha}} \tag{25}$$

Here $t^*_{\mathrm{pr}} = t_{\mathrm{pr}}/\tau$. This has been set up in a normalized form so that the initial reaction rate is the same as in (22), i.e.:

$$\frac{\mathrm{dO}^*_{\mathrm{ad}}}{\mathrm{d}t^*}(0) = k^*_0$$

Eq. (25) is slightly different from the non-normalized form used by Chen and Wake [4,5]. In terms of the present notation their equation can be written as:

$$\frac{\mathrm{dO}^*_{\mathrm{ad}}}{\mathrm{d}t^*} = \tilde{k}^*_0 \frac{1}{(t^*_{\mathrm{pr}}+t^*)^{\alpha}} \tag{26}$$

Eqs. (26) and (25) can be made identical by choosing:

$$\tilde{k}^*_0 = k^*_0 (t^*_{\mathrm{pr}})^{\alpha}$$

Eq. (25) is preferred here for two reasons: first it gives the standard isothermal rate of k^*_0 at $t^* = 0$, and secondly it approaches the constant non-diminishing case in the limit $t^*_{\mathrm{pr}} \to \infty$ (equivalent to the limit $b \to \infty$ in (22)). However (25) is not well behaved in the limit $t^*_{\mathrm{pr}} \to 0$ unless the extra assumption is made that $\tilde{k}^*_0 = k^*_0(t^*_{\mathrm{pr}})^{\alpha}$ is finite in that limit. When comparing our results with those of Chen and Wake [4,5] we will make this assumption also.

Eq. (25) can be solved by integrating, and using the initial conditions (23):

$$\mathrm{O}^*_{\mathrm{ad}} + \left(\frac{k^*_0 t^*_{\mathrm{pr}}}{1-\alpha} - \mathrm{O}^*_{\mathrm{ad0}}\right) = \frac{k^*_0 t^*_{\mathrm{pr}}}{1-\alpha}\left(\frac{1+t^*}{t^*_{\mathrm{pr}}}\right)^{1-\alpha} \tag{27}$$

Note that Eqs. (27) and (24) can be made identical by the substitutions:

$$1-\alpha = \frac{1}{\beta+1} \tag{28}$$

$$\left(\frac{k^*_0 t^*_{\mathrm{pr}}}{1-\alpha} - \mathrm{O}^*_{\mathrm{ad0}}\right) = b \tag{29}$$

$$t^*_{\mathrm{pr}} = \frac{\mathrm{O}^*_{\mathrm{ad0}} + b}{(\beta+1)k^*_0} \tag{30}$$

There is no problem in using (28) to relate α and β or in using (29) to relate k^*_0 and b. Eq. (30) imposes no extra restriction on parameter values as it can be derived from Eqs. (28) and (29).

4.3. CW model

Following the approach taken by Chen and Wake [4] the isothermal solution from (27) is now used to eliminate t^* from the governing Eq. (25), which becomes:

$$\frac{\mathrm{dO}^*_{\mathrm{ad}}}{\mathrm{d}t^*} = k^*_0\left(\frac{k^*_0 t^*_{\mathrm{pr}}(1+\beta)}{k^*_0 t^*_{\mathrm{pr}}(1+\beta) - \mathrm{O}^*_{\mathrm{ad0}} + \mathrm{O}^*_{\mathrm{ad}}}\right)^{\beta} \tag{31}$$

This equation is similar to that presented by Chen and Wake [4,5] but appears somewhat different because they made approximations equivalent to $t^*_{\mathrm{pr}} = 0$ and $\mathrm{O}^*_{\mathrm{ad0}} = 0$. It is possible to reconcile the two approaches in the limiting case $t^*_{\mathrm{pr}} \to 0$ by assuming $\tilde{k}^*_0 = k^*_0(t^*_{\mathrm{pr}})^{\alpha}$ remains finite. In this case Eq. (31) becomes:

$$\frac{\mathrm{dO}^*_{\mathrm{ad}}}{\mathrm{d}t^*} = \tilde{k}^*_0\left(\frac{\tilde{k}^*_0(1+\beta)}{\mathrm{O}^*_{\mathrm{ad}}}\right)^{\beta} \tag{32}$$

The right hand side of (32) is essentially the same as Eq. (17). The solution of Eq. (31) is:

$$\mathrm{O}^*_{\mathrm{ad}} - \mathrm{O}^*_{\mathrm{ad0}} + (1+\beta)k^*_0 t^*_{\mathrm{pr}} = (1+\beta)k^*_0 t^*_{\mathrm{pr}}\left[\frac{1+t^*}{t^*_{\mathrm{pr}}}\right]^{1/\beta+1} \tag{33}$$

4.4. Discussion

For the isothermal case discussed above, provided that the parameter values are set according to Eqs. (28) and (29), then the solutions from all three models ((24), (27) and (33)) are identical. However the key issue is how the three models behave in the non-isothermal case. The problem with using Eq. (33) instead of Eq. (24) for non-isothermal problems is the way in which the temperature dependence is introduced. In (24) we regard b as a constant parameter that is determined from fitting model results to experiments and does not depend on temperature. But for the non-isothermal case a general temperature-dependent rate coefficient k^* is used in place of the constant k^*_0. In (33) it is difficult to decide how to treat the term k^*_0 in the non-isothermal case. Chen and Wake [5] replace k^*_0 everywhere by the temperature-dependent coefficient k^*, which then appears inside the diminishing term. This form of temperature dependence was introduced by the particular method of derivation of Eq. (33). We suggest that there is no physical reason for replacing the constant parameter $b = k^*_0 t^*_{\mathrm{pr}}(1+\beta) - \mathrm{O}^*_{\mathrm{ad0}}$ by a temperature dependent function $b(T) = k^*(T)t^*_{\mathrm{pr}}(1+\beta) - \mathrm{O}^*_{\mathrm{ad0}}$. In our use of the non-isothermal version of Eq. (22) the parameter b will be treated as a temperature-independent constant. Results obtained using this approach and the approach of Chen and Wake [5] are compared below.

5. Temperature equation

The main point of the present work is to investigate the time predicted by the various models for a sample of coal to reach rapid self-heating. Therefore the coupled oxygen and energy conservation Eqs. (10) and (11), must both be solved together. The two equations can be combined and written in non-dimensional form as:

$$\frac{\mathrm{d}T^*}{\mathrm{d}t^*} = \sigma \frac{\mathrm{dO}^*_{\mathrm{ad}}}{\mathrm{d}t^*} \tag{34}$$

where

$$\sigma = \frac{Q\mathrm{O_D}}{C_p T_0}$$

Then Eq. (34) can be integrated, and after using the initial conditions, $\mathrm{O}^*_{\mathrm{ad}}(0) = \mathrm{O}^*_{\mathrm{ad0}}$ and $T^*(0) = 1$, we obtain:

$$T^* - 1 = \sigma(\mathrm{O}^*_{\mathrm{ad}} - \mathrm{O}^*_{\mathrm{ad0}}) \tag{35}$$

Following the notation used in the theory of thermal explosions [17], an alternative non-dimensional temperature can be introduced:

$$\theta = \frac{1}{\varepsilon}(T^* - 1) \tag{36}$$

where

$$\varepsilon = \frac{RT_0}{E_\mathrm{a}}$$

Combining (35) and (36) gives:

$$\theta = \nu(\mathrm{O}^*_{\mathrm{ad}} - \mathrm{O}^*_{\mathrm{ad0}}) \tag{37}$$

where

$$\nu = \frac{\sigma}{\varepsilon}$$

Note that

$$\frac{1}{T^*} = \frac{1}{1+\varepsilon\theta} = 1 - \frac{\varepsilon\theta}{1+\varepsilon\theta} \tag{38}$$

6. New model—non-isothermal case

Using (37) the non-isothermal version of Eq. (22) can be written as:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t^*} = \nu k^* \left(\frac{b+\mathrm{O}^*_{\mathrm{ad0}}}{b+\mathrm{O}^*_{\mathrm{ad}}}\right)^\beta = \nu \left(\frac{b+\mathrm{O}^*_{\mathrm{ad0}}}{b+\mathrm{O}^*_{\mathrm{ad}}}\right)^\beta A^*_0 \exp\left(-\frac{E_\mathrm{a}}{RT_0}\frac{1}{T^*}\right)$$

After some rearrangement using (37) and (38), this can be written as:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t^*} = \delta_0 \left(\frac{\lambda}{\lambda+\theta}\right)^\beta \exp\left(\frac{\theta}{1+\varepsilon\theta}\right) \tag{39}$$

Here:

$$\delta_0 = \nu k^*_0 = \nu A^*_0 \exp\left(-\frac{1}{\varepsilon}\right) \tag{40}$$

and

$$\lambda = \nu(\mathrm{O}^*_{\mathrm{ad0}} + b) = \frac{\delta_0(\mathrm{O}^*_{\mathrm{ad0}} + b)}{k^*_0} = \delta_0(1+\beta)t^*_{\mathrm{pr}} \tag{41}$$

Now the initial condition corresponding to $T^*(0) = 1$ is:

$$\theta(0) = 0 \tag{42}$$

In order to compare our results with those of Chen and Wake [4,5] an alternative constant $\tilde{\delta}_0$ is also introduced:

$$\tilde{\delta}_0 = \nu \tilde{k}^*_0 = \delta_0 (t^*_{\mathrm{pr}})^\alpha \tag{43}$$

In general, Eq. (39) cannot be solved analytically, but for the special case $\varepsilon \approx 0$ the resulting equation below can be solved:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t^*} = \delta_0 \left(\frac{\lambda}{\lambda+\theta}\right)^\beta \exp(\theta) \tag{44}$$

Note that typical parameter values for coal from Schmal et al. [12] and Sujanti et al. [18] give values for ε in the range (0.024–0.035), and therefore the approximation $\varepsilon \approx 0$ is reasonable.

6.1. Special case $\beta = 1$

In this case Eq. (44) becomes:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t^*} = \delta_0 \lambda \left(\frac{\exp(\theta)}{\lambda+\theta}\right)$$

This equation can be separated and integrated. Using the initial condition from (42) gives:

$$t^* = \frac{1}{\delta_0 \lambda}[(1+\lambda) - \exp(-\theta)\{1+\lambda+\theta\}] \tag{45}$$

It is not possible to invert this relationship to make it explicit in θ, but the limiting case $\theta \to \infty$ gives the time t^*_∞ at which the temperature grows without bound:

$$t^*_\infty = \frac{1}{\delta_0}\left(1 + \frac{1}{\lambda}\right) \tag{46}$$

In practice the onset of spontaneous combustion would be obvious well before $\theta \to \infty$ but the temperature rise is rapid and therefore the parameter t^*_∞ is a reasonable one to use for comparing all the models.

Using Eq. (41) with $\beta = 1$ gives $\lambda = 2\delta_0 t^*_{\mathrm{pr}}$ and then (46) becomes:

$$t^*_\infty = \frac{1}{\delta_0}\left(1 + \frac{1}{2\delta_0 t^*_{\mathrm{pr}}}\right) \tag{47}$$

For $\beta = 1$ then $\alpha = 1/2$, Eq. (43) gives $\tilde{\delta}_0 = \delta_0\sqrt{t^*_{\mathrm{pr}}}$ and (47) can be rewritten as:

$$t^*_\infty = \frac{\sqrt{t^*_{\mathrm{pr}}}}{\tilde{\delta}_0} + \frac{1}{2\tilde{\delta}^2_0} \tag{48}$$

Note that in the limit as $t^*_{\mathrm{pr}} \to \infty$ the right hand side of Eq. (25) is constant, i.e. the diminishing effect is not present, and (47) reduces to:

$$t^*_\infty = \frac{1}{\delta_0}$$

However, the corresponding limit of Eq. (48) is not defined.

Conversely in the limiting case $t_{\text{pr}}^* \to 0$, the limit of (47) is not defined but (48) reduces to:

$$t_\infty^* = \frac{1}{2\tilde{\delta}_0^2}$$

This is the same as the result derived by Chen and Wake [4,5].

6.2. General β

In the general case the separation of Eq. (44) gives:

$$(\lambda + \theta)^\beta \exp(-\theta)\mathrm{d}\theta = \delta_0 \lambda^\beta \,\mathrm{d}t^*$$

This equation can be simplified by making the substitution $\varphi = \theta + \lambda$, and it can then be integrated. Using the initial condition $\theta = 0$ at $t^* = 0$, gives:

$$t^* = \frac{1}{\delta_0}\lambda^{-\beta}\exp(\lambda)\int_\lambda^{\theta+\lambda}\varphi^\beta \exp(-\varphi)\,\mathrm{d}\varphi \tag{49}$$

The integral in Eq. (49) can be expressed in terms of incomplete Gamma functions (see [19]):

$$t^* = \frac{1}{\delta_0}\lambda^{-\beta}\exp(\lambda)[\gamma(\beta+1, \theta+\lambda) - \gamma(\beta+1, \lambda)] \tag{50}$$

Note for the special case $\beta = 1$ then $\gamma(2, x) = 1 - (1 + x)\exp(-x)$. Substituting in (50) this gives:

$$t^* = \frac{1}{\delta_0\lambda}\lambda\exp(\lambda)[-\{1+\theta+\lambda\}\exp(-\theta-\lambda) + \{1+\lambda\}\exp(-\lambda)]$$

With some rearrangement this equation can be shown to be the same as (45).

For the special case ($\beta = (1/2)$):

$$\gamma\left(\frac{3}{2}, x\right) = \frac{1}{2}\gamma\left(\frac{1}{2}, x\right) - \sqrt{x}\exp(-x) = \frac{\sqrt{\pi}}{2}\mathrm{erf}(\sqrt{x}) - \sqrt{x}\exp(-x)$$

Then Eq. (50) becomes:

$$t^* = \frac{1}{\delta_0\sqrt{\lambda}}\left[\exp(\lambda)\frac{\sqrt{\pi}}{2}\{\mathrm{erf}(\sqrt{\theta+\lambda}) - \mathrm{erf}(\sqrt{\lambda})\} - \sqrt{\theta+\lambda}\exp(-\theta) + \sqrt{\lambda}\right] \tag{51}$$

When $\theta \to \infty$ Eq. (51) gives:

$$t_\infty^* = \frac{1}{\delta_0\sqrt{\lambda}}\left[\exp(\lambda)\frac{\sqrt{\pi}}{2}\{\mathrm{erfc}(\sqrt{\lambda})\} + \sqrt{\lambda}\right]$$

For general β the limit $\theta \to \infty$ of Eq. (50) gives:

$$t_\infty^* = \frac{1}{\delta_0}\lambda^{-\beta}\exp(\lambda)[\Gamma(\beta+1) - \gamma(\beta+1, \lambda)]$$

Or

$$t_\infty^* = \frac{1}{\delta_0}\lambda^{-\beta}\exp(\lambda)[\Gamma(\beta+1, \lambda)] \tag{52}$$

The asymptotic form of Eq. (52) for large values of λ is (see [19]):

$$t_\infty^* = \frac{1}{\delta_0}\left[1 + \frac{\beta}{\lambda} + \frac{\beta(\beta-1)}{\lambda^2} + \cdots\right] \tag{53}$$

7. CW model—non-isothermal case

In order to compare our new version of the power-law model with previous work it is necessary to re-work some of it, using the same initial conditions throughout. In this section we investigate the version of the power-law model used by Chen and Wake [4,5]. Following their approach the non-isothermal version of Eq. (31) is:

$$\frac{\mathrm{dO}_{\text{ad}}^*}{\mathrm{d}t^*} = k^*\left(\frac{k^* t_{\text{pr}}^*(1+\beta)}{k^* t_{\text{pr}}^*(1+\beta) - \mathrm{O}_{\text{ad0}}^* + \mathrm{O}_{\text{ad}}^*}\right)^\beta \tag{54}$$

Note that we do not consider it to be correct to include the temperature-dependent k^* (rather than the constant k_0^*) within the diminishing part of the reaction, but nevertheless we will solve Eq. (54) for comparative purposes.

First we use Eq. (36) to express k^* in terms of θ:

$$k^* = A_0^*\exp\left(-\frac{E}{RT_0}\frac{1}{T^*}\right) = k_0^*\exp\left(\frac{\theta}{1+\varepsilon\theta}\right) \tag{55}$$

Then (54) becomes:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t^*} = \delta_0\left(1 + \left(\frac{\theta}{\lambda}\right)\exp\left(-\frac{\theta}{1+\varepsilon\theta}\right)\right)^{-\beta}\exp\left(\frac{\theta}{1+\varepsilon\theta}\right) \tag{56}$$

For the special case $\varepsilon \approx 0$ this simplifies to:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t^*} = \delta_0\left(\frac{\lambda}{\lambda + \theta\exp(-\theta)}\right)^\beta \exp(\theta) \tag{57}$$

7.1. Special case $\beta = 1$

In this case (57) becomes:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t^*} = \delta_0\lambda\left(\frac{\exp(2\theta)}{\lambda\exp(\theta) + \theta}\right) \tag{58}$$

In the alternative notation (58) can be written as:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t^*} = 2\tilde{\delta}_0^2\left(\frac{\exp(2\theta)}{2\tilde{\delta}_0\sqrt{t_{\text{pr}}^*}\exp(\theta) + \theta}\right) \tag{59}$$

In the limit $t_{\text{pr}}^* \to 0$ Eq. (59) reduces to:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t^*} = 2\tilde{\delta}_0^2\left(\frac{\exp(2\theta)}{\theta}\right) \tag{60}$$

Eq. (60) is the same as the equation solved by Chen and Wake [4,5].

However the approximation $t_{\text{pr}}^* \to 0$ is not necessary as the more general version, (58), can be separated and integrated.

After applying the initial conditions $\theta = 0$ at $t^* = 0$ we obtain:

$$t^* = \frac{1}{4\delta_0\lambda}[(1+4\lambda) - 4\lambda\exp(-\theta) - (1+2\theta)\exp(-2\theta)] \tag{61}$$

In the limit $\theta \to \infty$ Eq. (61) gives:

$$t^*_\infty = \frac{1}{\delta_0}\left(1 + \frac{1}{4\lambda}\right) \tag{62}$$

For the case $\beta = 1$ or $\lambda = 2\delta_0 t^*_{\mathrm{pr}}$ then (62) becomes:

$$t^*_\infty = \frac{1}{\delta_0}\left(1 + \frac{1}{8\delta_0 t^*_{\mathrm{pr}}}\right) \tag{63}$$

Eq. (63) can be rewritten as:

$$t^*_\infty = \frac{\sqrt{t^*_{\mathrm{pr}}}}{\tilde{\delta}_0} + \frac{1}{8\tilde{\delta}_0^2} \tag{64}$$

In the limit as $t^*_{\mathrm{pr}} \to \infty$, i.e. when the diminishing effect is not present, (63) reduces to the correct limit:

$$t^*_\infty = \frac{1}{\delta_0}$$

However, the corresponding limit of Eq. (64) is not defined. Conversely in the limiting case $t^*_{\mathrm{pr}} \to 0$, then Eq. (61) reduces to the form used by Chen and Wake [4,5], namely:

$$t^* = \frac{1}{8\tilde{\delta}_0^2}[1 - (1+2\theta)\exp(-2\theta)] \tag{65}$$

In the limit $\theta \to \infty$ Eq. (65) gives:

$$t^*_\infty = \frac{1}{8\tilde{\delta}_0^2}$$

This is the same as the limit of Eq. (64) as $t^*_{\mathrm{pr}} \to 0$.

Unfortunately Eq. (57) cannot be solved in closed form for general β.

8. Classical model—non-isothermal case

In this section the classical model with the time-dependent diminishing rate is re-worked. Using (36) and (40) the non-isothermal version of Eq. (25) can be written as:

$$\frac{d\theta}{dt^*} = \delta_0 \frac{1}{(1 + t^*/t^*_{\mathrm{pr}})^\alpha} \exp\left(\frac{\theta}{1+\varepsilon\theta}\right) \tag{66}$$

For the special case $\varepsilon \approx 0$, (66) becomes:

$$\frac{d\theta}{dt^*} = \delta_0 \frac{1}{(1 + t^*/t^*_{\mathrm{pr}})^\alpha} \exp(\theta) \tag{67}$$

8.1. *Special case β = 1, α = 1/2*

For this case Eq. (67) can be separated and integrated:

$$t^* = \frac{1}{4\delta_0^2 t^*_{\mathrm{pr}}}[\{1-\exp(-\theta)\}^2 + 4\delta_0 t^*_{\mathrm{pr}}\{1-\exp(-\theta)\}] \tag{68}$$

Using $\tilde{\delta}_0 = \delta_0\sqrt{t^*_{\mathrm{pr}}}$, (68) can be rewritten as:

$$t^* = \frac{1}{4\tilde{\delta}_0^2}[\{1-\exp(-\theta)\}^2 + 4\tilde{\delta}_0\sqrt{t^*_{\mathrm{pr}}}\{1-\exp(-\theta)\}] \tag{69}$$

Note that in the limit $t^*_{\mathrm{pr}} \to 0$ Eq. (69) becomes:

$$t^* = \frac{1}{4\tilde{\delta}_0^2}[1-\exp(-\theta)]^2 \tag{70}$$

This is the same as the equation given by Chen and Wake [5]. The limit $\theta \to \infty$ in Eq. (68) gives:

$$t^*_\infty = \frac{1}{\delta_0}\left(1 + \frac{1}{4\delta_0 t^*_{\mathrm{pr}}}\right) \tag{71}$$

The Chen and Wake [5] version of Eq. (71), obtained from the limit $\theta \to \infty$ in Eq. (70), is:

$$t^*_\infty = \frac{1}{4\tilde{\delta}_0^2}$$

8.2. *General β*

Now the integration of Eq. (67), together with the initial condition from (42) gives:

$$t^* = t^*_{\mathrm{pr}}\left[-1 + \left\{1 + \frac{1-\alpha}{\delta_0 t^*_{\mathrm{pr}}}(1-\exp(-\theta))\right\}^{1/1-\alpha}\right] \tag{72}$$

In the limit $\theta \to \infty$ Eq. (72) gives:

$$t^*_\infty = \frac{1}{\delta_0}\frac{\lambda}{(1+\beta)}\left[-1 + \left\{1 + \frac{1}{\lambda}\right\}^{\beta+1}\right] \tag{73}$$

The asymptotic form of (73) for large values of λ is:

$$t^*_\infty = \frac{1}{\delta_0}\left[1 + \frac{\beta}{2\lambda} + \frac{\beta(\beta-1)}{6\lambda^2} + \cdots\right] \tag{74}$$

9. Elovich model

For comparative purposes the Elovich model is also considered here. The corresponding equation can also be solved in closed form using the same approximations as used above. The normalized form of the Elovich equation (see Eq. (12)) can be written in non-dimensional form as follows:

$$f(\mathrm{O}^*_{\mathrm{ad}}) = \exp(-b^*(\mathrm{O}^*_{\mathrm{ad}} - \mathrm{O}^*_{\mathrm{ad0}}))$$

Then the corresponding equation for the non-dimensional temperature θ is:

$$\frac{d\theta}{dt^*} = \delta_0 \exp(-\eta\theta)\exp\left(\frac{\theta}{1+\varepsilon\theta}\right) \tag{75}$$

Here $\eta = b^*/\nu$. As above the approximation $\varepsilon \approx 0$ is made, so that Eq. (75) can be solved in the form:

$$t^* = \frac{1}{\delta_0(1-\eta)}[1 - \exp(-[1-\eta]\theta)] \tag{76}$$

Table 1
Comparison between models

Model name	t^*_∞	t^*_∞ (Alternative notation)	t^*_∞ (Alternative notation, $t^*_{\text{pr}} \to 0$)
Constant reaction rate	$\frac{1}{\delta_0}$	$\frac{\sqrt{t^*_{\text{pr}}}}{\tilde{\delta}_0}$	Not applicable
New model power-law rate	$\frac{1}{\delta_0}\left(1+\frac{1}{2\delta_0 t^*_{\text{pr}}}\right)$	$\frac{\sqrt{t^*_{\text{pr}}}}{\tilde{\delta}_0}+\frac{1}{2\tilde{\delta}_0^2}$	$\frac{1}{2\tilde{\delta}_0^2}$
CW model power-law rate	$\frac{1}{\delta_0}\left(1+\frac{1}{8\delta_0 t^*_{\text{pr}}}\right)$	$\frac{\sqrt{t^*_{\text{pr}}}}{\tilde{\delta}_0}+\frac{1}{8\tilde{\delta}_0^2}$	$\frac{1}{8\tilde{\delta}_0^2}$
Classical model time-dependent rate	$\frac{1}{\delta_0}\left(1+\frac{1}{4\delta_0 t^*_{\text{pr}}}\right)$	$\frac{\sqrt{t^*_{\text{pr}}}}{\tilde{\delta}_0}+\frac{1}{4\tilde{\delta}_0^2}$	$\frac{1}{4\tilde{\delta}_0^2}$
Elovich [15,16]	$\frac{1}{\delta_0(1-\eta)}$	$\frac{\sqrt{t^*_{\text{pr}}}}{\tilde{\delta}_0(1-\eta)}$	Not applicable

Special case $\beta = 1$. Note that $\tilde{\delta}_0 = \delta_0\sqrt{t^*_{\text{pr}}}$.

In the limit $\theta \to \infty$ Eq. (76) gives:

$$t^*_\infty = \frac{1}{\delta_0(1-\eta)}$$

10. Comparison of results and conclusions

The key parameter to consider is the time t^*_∞ at which self-ignition occurs, given by the limit $\theta \to \infty$. The results for the special case $\beta = 1$ are shown in Table 1, with the solution for the constant reaction rate included as the baseline. The results show that our power-law model predicts a longer time to ignition than either the classical model with a time-dependent right hand side or the power-law model introduced by Chen and Wake [4]. This conclusion is confirmed by the plots of time versus temperature in Fig. 1.

The results shown are for the special case $\beta = 1$ but the asymptotic formulae (see Eqs. (53) and (74) and Table 2) for general β show that the relative order of times to reach ignition for the models does not depend on β. If the value of λ (defined in Eq. (41)) is increased then the curves in Fig. 1 move closer together and conversely if λ is decreased they spread further apart. This effect is shown for the power-law model in Fig. 2.

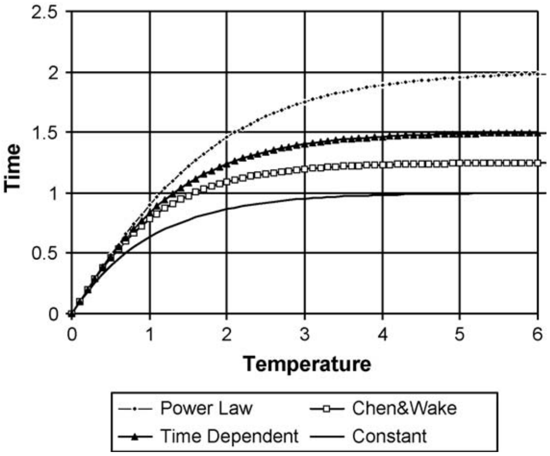

Fig. 1. Plots of normalized time ($t^*\delta_0$) vs. dimensionless temperature (θ) for the case $\beta = 1$ and $\lambda = 1$.

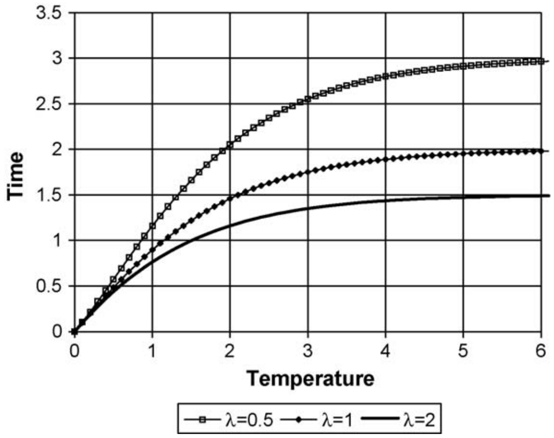

Fig. 2. Plots of normalized time ($t^*\delta_0$) vs. dimensionless temperature (θ) for the power law model. $\beta = 1$ and various λ values.

Table 2
Comparison between models

Model name	β	α	$t^*_\infty\delta_0$
Constant reaction rate			1
New model power-law rate	1	1/2	$1+\frac{1}{\lambda}$
	1/2	1/3	$1+\frac{\sqrt{\pi}}{2\sqrt{\lambda}}\exp(\lambda)\,\mathrm{erfc}(\sqrt{\lambda})$
	β	$\frac{\beta}{1+\beta}$	$\lambda^{-\beta}\exp(\lambda)\left[\Gamma(\beta+1)-\gamma(\beta+1,\lambda)\right] \approx 1+\beta/\lambda+\beta(\beta-1)/\lambda^2+\cdots$
Classical model—time-dependent rate	β	$\frac{\beta}{1+\beta}$	$\frac{\lambda}{(\beta+1)}\left[-1+\left\{1+\frac{1}{\lambda}\right\}^{\beta+1}\right] \approx 1+\beta/2\lambda+\beta(\beta-1)/6\lambda^2+\cdots$

General β. Note that $\lambda = \delta_0(1+\beta)t^*_{\text{pr}}$.

From the comparison of the results given in Tables 1 and 2 it is not possible to gain support for preferring one model rather than the others. All the models behave reasonably and there is sufficient uncertainty in parameter values so that a comparison with experimental results is unlikely to help. However we claim that our new power-law model is more physically based and should be preferred. Unfortunately experimental data are not available that would allow a comparison of the model proposed here with other simple lumped parameter models such as the Elovich model, or with more complex three-dimensional models.

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